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Synthesis of Bis(phospha-λ^5-azenes) by a Redox–Condensation Reaction. Formation of an Anomalous *N*-Cyanophospha-λ^5-azene from Urea

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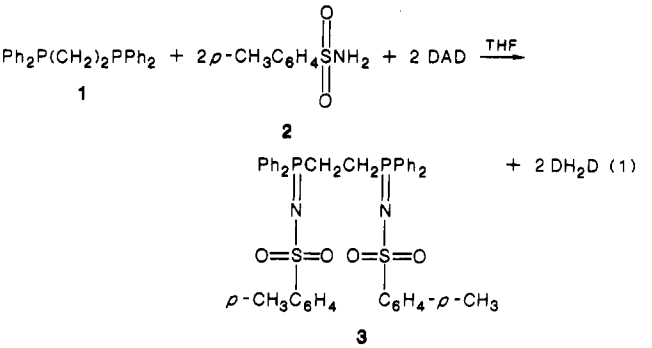
The reaction of diphosphines [$Ph_2P(CH_2)_nPPh_2$; n = 1, 2] with sulfonamides, a phosphinamide, and cyanamide as well as of a dicarboxamide, a disulfonamide, urea, thiourea, and sulfamide with triphenylphosphine in the presence of diethyl azodicarboxylate has been shown to produce bis(phospha-λ^5-azenes). In the case of cyanamide with bis(diphenylphosphino)methane a mono- (**10**) as well as a bis(phospha-λ^5-azene) (**9**) could be prepared. Further, the monophospha-λ^5-azene monooxide **11** was also isolated. In the case of thiourea, the monophospha-λ^5-azene intermediate was also isolated. The reaction of urea with bis(diphenylphosphino)methane gave the mono-*N*-cyanophospha-λ^5-azene monooxide (**11**) along with bis(diphenylphosphino)methane dioxide. This is the first observation of a nitrile produced in the reaction of an amide, a phosphine, and diethyl azodicarboxylate at room temperature.

The use of the redox–condensation system diethyl azodicarboxylate (DAD)–triphenylphosphine (TPP) for the preparation of *N*-acyl-, *N*-sulfonyl-, and *N*-phosphinylphospha-λ^5-azenes has recently been reported.[2-5] This new phospha-λ^5-azene synthesis is quite remarkable in the sense that the reaction occurs directly between the two partners (TPP and RNH_2, R = acyl, sulfonyl, and phosphinyl) without the need for activated derivatives, as in the classical methods.[6-8]

Since both linear and cyclic bis(phospha-λ^5-azenes) are interesting and important compounds, we decided to see whether this new phospha-λ^5-azene synthetic methodology could be extended to the preparation of these systems. This paper reports on the preparation of linear bis(phospha-λ^5-azenes) using this method and attempts at preparing cyclic systems, one of which gave a rather unusual result.

Results and Discussion

Reaction of Diphosphines with Monoamides. Reaction of 1 equiv of 1,2-bis(diphenylphosphino)ethane (**1**) with 2 equiv of *p*-toluenesulfonamide (**2**) and 2 equiv of diethyl azodicarboxylate (DAD) in dry THF at 0 °C (eq 1) produced the bis(phospha-λ^5-azene) **3** in good yield



(Table I), along with diethyl hydrazinedicarboxylate (DH_2D). A similar reaction (eq 2) took place when di-

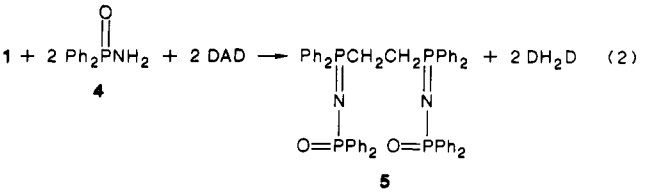


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Table I. Some Physical and Spectroscopic Data of the Phosphaazenes

phospha-λ^5-azene	recryst solvent	mp (°C)	yield (%)	IR (cm^{-1})
3	Me_2SO	279	48	1580 (Ar); 1260 (SO_2); 1160 (P=N); 820 (S—N)[a]
5	2-propanol–water	260[b]	52	1270 (P=N); 1180 (P=O); 1030[a]
7	MeCN	194–196[c]	83	2176 (C≡N); 1586; 1481 (Ar); 1435 (P—C); 1269 (P=N); 1115[d]
9	methanol	249–251	75	2180 (C≡N); 1590; 1480 (Ar); 1435 (P—C); 1285 (P=N); 1115[e]
10	chloroform–hexane	118–120	45	2175 (C≡N); 1585; 1480 (Ar); 1435 (P—C); 1280 (P=N); 1110[f]
11	chloroform	189–191	60	2187 (C≡N); 1435 (P—C); 1285 (P=N); 1193 (P=O); 1119[e]
14	2-propanol	180–182	61	1650 (C=O); 1570; 1480 (Ar); 1340 (P=N)[a]
16	methanol–chloroform	219	57	1260 (SO_2); 1140 (P=N); 825 (S—N)[a]
17b	ethanol	161–162	73	3400, 3260, 3160 (NH); 1615 (C=S); 1155 (P=N)[a]
18a	ethanol	202	46	1650 (C=O); 1310 (P=N)[a]
18b	petroleum ether	159–160	52	1600 (C=S); 1160 (P=N)[a]
18c	ethanol	243–244[g]	86	1590, 1480 (Ar); 1245 (SO_2); 1115 (P=N); 810 (S—N)[a]

[a] Nujol mull. [b] Lit.[17] mp 262–264 °C. [c] Lit.[10] mp 196 °C. [d] Diffuse reflectance spectrum in KBr powder. [e] KBr pellet. [f] Neat film [g] Lit.[18] mp 245–246 °C and 242–244 °C.

phenylphosphinamide (**4**) was used in place of **2**. The bis(phosphinylphospha-λ^5-azene) (**5**) was obtained in 52% yield (Table I). In these cases structure proof rested on IR and ^1H NMR spectroscopy and elemental analyses.

Reaction of a Diphosphine with Cyanamide (6). We have also recently discovered[9] that cyanamide (**6**) can react with a phosphine in the presence of DAD to produce an *N*-cyanophospha-λ^5-azene. Thus, TPP and DAD react with **6** to give *N*-cyano-*P,P,P*-triphenylphospha-λ^5-azene (**7**)[10] while reaction of bis(diphenylphosphino)methane (**8**)

$$Ph_3P{=}NCN$$
7

with a 2-fold excess (4 equiv) of cyanamide (**6**) and DAD (4 equiv) resulted in the bis(phospha-λ^5-azene), **9** (eq 3).

$$\underset{\mathbf{8}}{Ph_2PCH_2PPh_2} + \underset{\mathbf{6}}{H_2NCN\ (4\ equiv)} \xrightarrow{DAD\ (4\ equiv)} \underset{\mathbf{9}}{Ph_2P(NCN)CH_2P(NCN)Ph_2} \quad (3)$$

In addition, the use of 1 equiv each of **6** and DAD resulted in the monophospha-λ^5-azene **10** in 45% yield along with recovered **8** (10%) and 25% of a compound we have identified as the monophospha-λ^5-azene monooxide **11** (eq 4). It should also be pointed out that a small amount of

$$\underset{\mathbf{8}}{} + \underset{\mathbf{6}}{H_2NCN\ (1\ equiv)} \xrightarrow{DAD} \underset{\mathbf{10}}{Ph_2P(NCN)CH_2PPh_2} + \underset{\mathbf{11}}{Ph_2P(NCN)CH_2P(O)Ph_2} \quad (4)$$

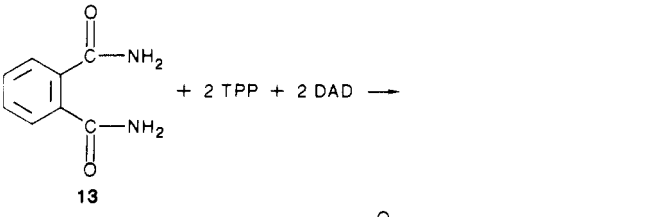
this oxide (**11**; 8%) was found even when 4 equiv of cyanamide was used (vide supra). Further, interestingly, reaction of 1 equiv of **8** with 2 equiv each of **6** and DAD resulted in the oxide **11** being the major product (60%) with a lesser amount (9%) of the bis(phospha-λ^5-azene) **9**.

Structure proofs for compounds **9**, **10**, and **11** rest on IR (Table I), ^{31}P, ^{13}C, and ^1H NMR spectra, by comparison with triphenylphosphine oxide, *N*-cyano-*P,P,P*-triphenylphospha-λ^5-azene (**7**), and dioxide **12**, and elemental analyses. Thus, for example, $\delta_{^{31}P}$ for **7** is 25.07, for **8** it

$$\underset{\mathbf{12}}{Ph_2P(O)CH_2P(O)Ph_2} \qquad \underset{\text{TPPO}}{Ph_3P{=}O}$$

is −21.07, for the dioxide **12** it is 25.47, and for triphenylphosphine oxide (TPPO) it is 29.76. Compound **9** shows a single ^{31}P absorption at δ 22.83, compound **10** shows an AX pair of doublets at δ 27.43 (>P=N) and −28.70 (>P:) (J = 57.4 Hz), and compound **11** shows an AX pair of doublets at δ 24.17 and 23.11 (J = 12.0 Hz). Since the ^{31}P in **7** is shielded relative to that in TPPO, the peak at 23.11 in **11** tentatively is assigned to the phospha-λ^5-azene phosphorus and the one at 24.17 to the oxide phosphorus. The C≡N stretch for compounds **9**–**11** appeared in the IR spectra at 2175–2187 cm^{-1} and the P=N stretch at 1280–1285 cm^{-1}.

Reaction of Dicarboxamides and Disulfonamides with Monophosphines. The alternative to the above reaction, namely the reaction of diamides with monophosphines, was examined and also found to yield bis(phospha-λ^5-azenes) (Table I). Thus, the reaction of phthalamide (**13**) with 2 equiv of TPP and DAD produced the bis(phospha-λ^5-azene) **14** (eq 5) in 61% yield (Table



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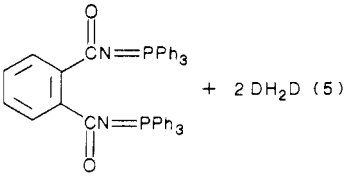

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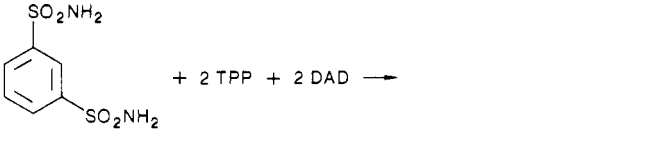

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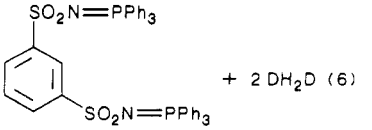

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I). A similar reaction with *m*-benzenedisulfonamide (**15**) gave a quite good yield of the bis(sulfonylphospha-λ^5-azene) **16** (eq 6; Table I). Even more interesting were the reactions of phosphines with urea, thiourea, and sulfamide (Table I). When 2 equiv each of TPP and DAD were used, bis(phospha-λ^5-azenes) (**18a–c**) were isolated in good to excellent yield. In the case of thiourea, reaction with 1 equiv each of TPP and DAD gave the monophospha-λ^5-azene (**17b**) in 73% yield. With urea and sulfamide, al-

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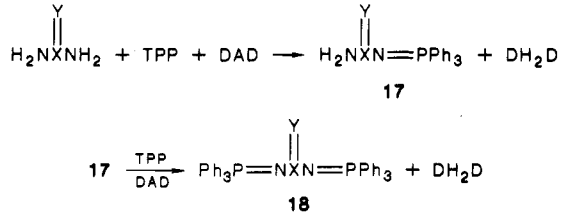
Scheme I[a]



[a] **a**, X = C; Y = O; **b**, X = C; Y = S; **c**, X = S=O; Y = O.

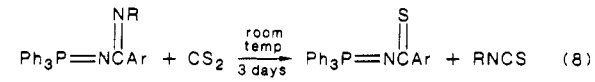
though the monoadducts were not isolated, there was NMR evidence that they were formed initially in the reaction. Scheme I shows these reactions.

We previously showed that the reaction of carboxamides with TPP and DAD required either an aromatic carboxamide or an aliphatic amide with an electron-withdrawing substituent on the alkyl group.[3] We can now add urea, thiourea, and cyanamide to the list of reactive amides. It should additionally be pointed out that this list also includes one other example of a substituted urea, namely azodicarbonamide, reacting with phosphines.[11] We also note that the NH_2 group is primarily electron-donating by resonance but inductively electron-withdrawing. In addition, the monophosphazene adducts **17a–c** are reactive amides and yet the phosphazenyl nitrogen must be primarily electron-donating into the carbonyl. Thus, these results taken with the previous results which showed that simple alkyl carboxamides do not react and those amides with electron-withdrawing substituents do react,[3] do not allow one to come to any conclusions about the mechanistic subtleties of this reaction.

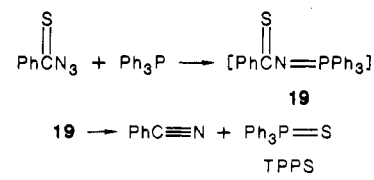
A very significant observation is that thiourea reacts to form **17b** and **18b**, which are phospha-λ⁵-azenes of the type $R(S)CN{=}PR'_3$. Until recently compounds of this type were unknown although they had been postulated as intermediates in the reactions between thiocarbonyl compounds and phosphines.[12,13] For example, thiobenzoyl azide reacts with TPP to produce benzonitrile and triphenylphosphine sulfide (TPPS), and the phosphazene, **19**, was postulated as the intermediate (Scheme II). It has also been shown that, contrary to the course of the reaction of carboxamides with TPP and DAD,[2,3] and of phosphines with azodicarbonamide[11] which produce *N*-acylphospha-λ⁵-azenes, *N*-(thioacyl)amides are converted to nitriles in the presence of DAD and TPP[14] (eq 7).

The reasons for the apparent greater stability of *N*-acylphospha-λ⁵-azenes, which decompose to nitriles only at elevated temperatures,[3,15] compared to the *N*-(thioacyl)phospha-λ⁵-azenes are at present not clear. Indeed, as will be shown below, we have uncovered the first example of the production of a nitrile from what must be an amide intermediate.

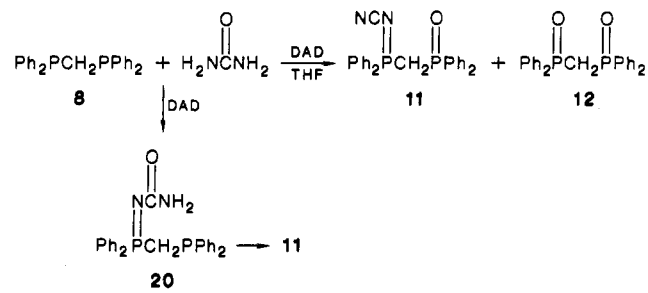
The recent report of the isolation of *N*-(thioacyl)phospha-λ⁵-azenes involved reaction of the phospha-λ⁵-azene derived from an amidine with a very large excess of CS_2 for 4 days (eq 8).[16]



Scheme II



Scheme III



Reaction of Urea with Bis(diphenylphosphino)methane (8). The possibility of obtaining new and novel phosphorus–nitrogen heterocycles containing two phospha-λ⁵-azene linkages by reaction of diamides with diphosphines in the presence of DAD was explored next.

The reaction of bis(diphenylphosphino)methane (8) with 1 equiv each of urea and DAD provided a mixture of two main phosphorus-containing products. Purification by chromatography provided, in the earlier fractions, a compound identified as the monooxide monophospha-λ⁵-azene **11** and in later fractions the dioxide **12**. Yields varied but were approximately 30–40% of each (Scheme III).

This is a rather interesting reaction. It is the first time a nitrile has been obtained from an amide at room temperature. It must be formed via the intermediate **20** and the intramolecular nature of the second dehydration must render it favorable relative to its intermolecular counterpart. This is because **17a** does not produce **7** but rather goes on to give **18a**.

Studies are currently underway on the reaction of urea with other diphosphines in order to see whether this reaction is unique.

Experimental Section

General Methods. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer Model 377 or 599B dispersive spectrophotometers or a Biorad-Digilab FTS-40 FT-IR spectrophotometer. The diffuse reflectance spectra were done in KBr powder by using a Spectra Tech DRIFTS accessory. NMR spectra were taken on a Varian XL-100, EM-360, or Nicolet NT-200 WB instrument as solutions in $CDCl_3$ (except where noted) using tetramethylsilane as internal standard for ^1H and ^{13}C. External H_3PO_4 was the standard for ^{31}P NMR spectra. ^{13}C and ^{31}P spectra were recorded by using ^1H decoupling. UV spectra were taken on a Perkin-Elmer 402 instrument. Elemental analyses were determined by the Microanalytical Labs at the Hebrew University in Jerusalem or Texas Analytical Laboratories, Houston, TX. Diphenylphosphinamide was prepared by the method of Kreutzkamp and Schindler[19] while other amides and sulfonamides were prepared by standard procedures. THF was distilled from $LiAlH_4$ immediately prior to use. All reactions were

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executed under an atmosphere of dry nitrogen or argon, using oven-dried glassware.

1,2-Bis[*N*-(*p*-tolylsulfonyl)-*P*,*P*-diphenylphospha-λ⁵-azenyl]ethane (3). To a suspension of *p*-toluenesulfonamide **2** (1.36 g, 8 mmol) and 1,2-bis(diphenylphosphino)ethane (**1**, 1.59 g, 4 mmol) in THF (10 mL) at 0 °C was added a solution of diethyl azodicarboxylate (1.39 g, 8 mmol) in THF (5 mL) dropwise with stirring. During the addition, the solution cleared and after 5 min a precipitate formed. The mixture was stirred for an additional 30 min at room temperature and filtered, and the crude product was recrystallized from dimethyl sulfoxide: yield 1.17 g (40%), mp 279 °C; ^{1}H NMR ($CDCl_3$ + CF_3COOD) δ 2.3 (s, 6 H, CH_3Ar), 2.8 (d, 4 H, J = 13 Hz, CH_2P), 6.8–7.7 (m, 28 H, Ar H). Anal. Calcd for $C_{40}H_{38}N_2O_4S_2P_2$: C, 65.20; H, 5.19; N, 3.80; P, 8.40. Found: C, 65.48; H, 5.09; N, 3.67; P, 8.34.

1,2-Bis[*N*-(diphenylphosphinyl)-*P*,*P*-diphenylphospha-λ⁵-azenyl]ethane (5). Using the procedure described above, diphenylphosphinamide (**4**, 1.36 g, 8 mmol) was reacted with 1,2-bis(diphenylphosphino)ethane (**1**, 1.59 g, 4 mmol) and DAD (1.39 g, 8 mmol). The product was purified by chromatography on silica gel using ethyl acetate/petroleum ether (1:1) and recrystallized from 2-propanol–water: yield 1.6 g (52%), mp 260 °C (lit.[17] mp 262–264 °C); ^{1}H NMR ($CDCl_3$ + CF_3COOD) δ 2.8 (d, 4 H, CH_2P), 7.1–7.9 (m, 40 H, Ar H); UV (methanol) λ_{max} 265 nm (log ε = 3.63).

***N*-Cyano-*P*,*P*,*P*-triphenylphospha-λ⁵-azene (7).** To a stirred solution of 1.31 g (5 mmol) of triphenylphosphine and 210 mg (5 mmol) of cyanamide (**6**) in 10 mL of dry THF was added a solution of 870 mg (5 mmol) of DAD slowly, under N_2, at 5–10 °C. A white precipitate formed quickly and the mixture was stirred overnight and filtered to give 1.25 g (83%) of **7**: mp 194–196 °C (lit.[10] mp 196 °C); ^{31}P NMR ($CDCl_3$) δ 25.07 (lit.[10] 23.1); ^{13}C NMR ($CDCl_3$) δ 133.39 (d, para C, J = 2.9 Hz), 132.48 (d, ortho C, J = 10.4 Hz), 129.19 (d, meta C, J = 12.8 Hz), 126.69 (d, ipso C, J = 103.6 Hz), 118.70 (s, -*C*≡N) [lit.[10] δ (*J*) 133.5 (4 Hz), 132.4 (11 Hz), 129.3 (13 Hz), 126.7 (104 Hz), 118.7]. Recrystallization from MeCN gave 900 mg (60%), mp 194–196 °C.

Bis(*N*-cyano-*P*,*P*-diphenylphospha-λ⁵-azenyl)methane (9). To a stirred solution of 770 mg (2 mmol) of bis(diphenylphosphino)methane (**8**) and 336 mg (8 mmol) of cyanamide (**6**) in 25 mL of dry THF, at 0–5 °C, under nitrogen, was added a solution of 697 mg (4 mmol) of DAD in 5 mL of dry THF. The mixture was stirred at room temperature for 24 h and a white precipitate formed which was filtered and washed with 25 mL of THF. Recrystallization from MeOH gave 700 mg of bis(*N*-cyano-*P*,*P*-diphenylphospha-λ⁵-azenyl)methane (**9**): mp 249–251 °C; ^{1}H NMR (Me_2SO-d_6) δ 4.94 (t, 2 H, CH_2, J = 14.2 Hz), 7.4–7.9 (m, 20 H, Ar H); ^{31}P NMR (Me_2SO-d_6) δ 22.83; ^{13}C NMR (Me_2SO-d_6) δ 24.67 (t, CH_2, J = 65.2 Hz), 116.33 (s, *C*≡N), 127.05 (d, C-1 in PhP, J = 104.2 Hz), 128.88 [t, C-3 in PhP, J (outer peak spacing) = 12.9 Hz], 131.21 [t, C-2 in PhP, J (outer peak spacing) = 10.9 Hz], 133.15 (s, C-4 in Ph–P). Anal. Calcd for $C_{27}H_{22}N_4P_2$: C, 69.82; H, 4.78; N, 12.06. Found: C, 69.79; H, 4.77; N, 12.03.

Concentration of the mother liquor from the recrystallization gave a solid which was recrystallized from $CHCl_3$ to produce 70 mg (8%) of the monooxide monophospha-λ⁵-azene **11** mp 189–191 °C (vide infra).

(*N*-Cyano-*P*,*P*-diphenylphospha-λ⁵-azenyl)(diphenylphosphino)methane (10). To a stirred solution of 84 mg (2 mmol) of cyanamide (**6**) and 770 mg (2 mmol) of bis(diphenylphosphino)methane (**8**) in 20 mL of dry THF, under argon, was added, by syringe, 348 mg (2 mmol) of DAD, at 0–5 °C. The solution was stirred overnight at room temperature and the solvent was removed under a stream of argon. The crude product was separated by preparative, centrifugally accelerated, radial thin-layer chromatography, using a Harrison Research Model 7924T chromatotron using silica gel 60 PF_{254} (EM Science) and $CHCl_3$ to elute. There were 80 mg of recovered **8** (10%), 380 mg of **9** (45%) and 220 mg of the monooxide monophospha-λ⁵-azene **11** (25%). The (*N*-cyanodiphenyl-*P*,*P*-phospha-λ⁵-azenyl)(diphenylphosphino)methane (**10**) was recrystallized from $CHCl_3$/hexane: mp 118–120 °C; ^{1}H NMR ($CDCl_3$) δ 3.25 (d, 2 H, CH_2, J = 14 Hz), 7.1–8.0 (m, 20 H, Ar H); ^{31}P NMR ($CDCl_3$) δ 24.43 (d, *P*═NCN, J = 57.4 Hz), −28.70 (d, Ph_2PCH_2, J = 57.4 Hz); ^{13}C NMR ($CDCl_3$) δ 28.34 (dd, CH_2, J = 69.3 Hz, 36.0 Hz), 118.56 (s, *C*≡N), 126.86 (d, C-1 in PhP═N, J = 99.3 Hz), 128.77 (d, C-3 in PhP═N, J = 15.6 Hz), 128.76 (s, C-4 in Ph_2PCH_2), 129.25 (d, C-3 in Ph_2PCH_2, J = 7.8 Hz), 131.50 (dd, C-2 in PhP═N, J = 10.2 Hz, 1.6 Hz), 132.70 (d, C-2 in Ph_2PCH_2, J = 20.9 Hz), 133.18 (d, C-4 in PhP═N, J = 2.9 Hz), 136.43 (dd, C-1 in Ph_2PCH_2, J = 14.3 Hz, 7.6 Hz). Anal. Calcd for $C_{26}H_{22}N_2P_2$: C, 73.58; H, 5.23; N, 6.60. Found: C, 73.60; H, 5.24; N, 6.58.

Reaction of Bis(diphenylphosphino)methane (8) with 2 Equiv of Cyanamide (6). To a well-stirred and cooled (0–5 °C) solution of 697 mg (4 mmol) of DAD in 20 mL of dry THF were added dropwise from 2 syringes, simultaneously, solutions of bis(diphenylphosphino)methane (**8**; 770 mg; 2 mmol) in 5 mL of dry THF and cyanamide (**6**; 168 mg, 4 mmol) in 5 mL of dry THF, under nitrogen. The reaction mixture was stirred 24 h at room temperature, the solvent was removed with a stream of air, and the crude product was purified by column chromatography (silica gel, EtOAc/EtOH eluent). The first solid fraction was recrystallized from $CHCl_3$ to give 525 mg (60%) of [(*N*-cyano-*P*,*P*-diphenylphospha-λ⁵-azenyl)methyl]diphenylphosphine oxide (**11**): mp 189–191 °C; ^{1}H NMR ($CDCl_3$) δ 3.70 (dd, 2 H, CH_2, J = 15.8 Hz, 12.7 Hz), 7.2–8.2 (m, 20 H, Ar H); ^{31}P NMR ($CDCl_3$) δ 23.11 (d, *P*═N, J = 12.0 Hz), 24.17 (d, *P*═O, J = 12.1 Hz); ^{13}C NMR ($CDCl_3$) δ 31.56 (dd, CH_2, J = 57.5 Hz, 55.1 Hz), 118.38 (br s, *C*≡N), 125.94 (dd, C-1 of PhP═N, J = 103.6 Hz, 2.1 Hz), 128.78 (d, C-3 of PhP═O, J = 12.5 Hz), 128.89 (d, C-3 of PhP═N, J = 13.3 Hz), 130.47 (d, C-2 of PhP═O, J = 9.9 Hz), 131.79 (dd, C-1 of PhP═O, J = 104.5 Hz, 3.9 Hz), 132.14 (d, C-2 of PhP═N, J = 10.9 Hz), 132.18 (d, C-4 of PhP═O, J = 3.0 Hz), 133.31 (d, C-4 of PhP═N, J = 3.1 Hz). See below for elemental analysis.

The second solid fraction was recrystallized from ethanol to give 85 mg (9%) of bis(*N*-cyano-*P*,*P*-diphenylphospha-λ⁵-azenyl)methane (**9**), mp 245–247 °C.

***N*,*N*′-*o*-Phthaloylbis(*P*,*P*,*P*-triphenylphospha-λ⁵-azene) (14).** To a cold solution of *o*-phthalamide (**13**, 0.41 g, 2.5 mmol) and triphenylphosphine (1.31 g, 5 mmol) in THF (15 mL) was added a solution of DAD (0.87 g, 5 mmol) in THF (5 mL). After stirring at room temperature for 24 h, the solvent was evaporated in vacuo and the residual mixture separated on a dry alumina column (activated with 3% H_2O). The product was eluted with ether and recrystallized from 2-propanol: yield 1.0 g (61%), mp 180–182 °C; ^{1}H NMR (Me_2SO-d_6) 7.1–7.9 (m, Ar H). Anal. Calcd for $C_{44}H_{34}N_2O_2P_2$: C, 77.18; H, 5.00; N, 4.09; P, 9.04. Found: C, 77.22; H, 5.21; N, 4.15; P, 8.92.

***N*,*N*′-(*m*-Phenylenedisulfonyl)bis(*P*,*P*,*P*-triphenylphospha-λ⁵-azene) (16).** Using the same procedure described above for **14**, *m*-benzenedisulfonamide (**15**, 0.59 g, 2.5 mmol) was reacted with triphenylphosphine (1.31 g, 5 mmol) and DAD (0.87 g, 5 mmol). The product (1.07 g, 57%) was recrystallized from methanol–chloroform: mp 219 °C; ^{1}H NMR (Me_2SO-d_6) δ 6.8–7.9 (m, Ar H). Anal. Calcd for $C_{42}H_{34}N_2O_4S_2P_2$: C, 66.53; H, 4.52; N, 3.69; P, 8.17. Found: C, 66.58; H, 4.46; N, 3.52; P, 8.30.

***N*-(Thiocarbamoyl)-*P*,*P*,*P*-triphenylphospha-λ⁵-azene (17b).** To a suspension of thiourea (0.76 g, 10 mmol) and TPP (2.62 g, 10 mmol) in anhydrous THF (20 mL) was added dropwise a solution of DAD (1.74 g, 10 mmol) in THF (8 mL). After stirring at room temperature for 24 h, the solvent was removed in vacuo and the semisolid residue was washed several times with ether and then with water. The remaining material was recrystallized from ethanol: yield 2.45 g (73%), mp 161–162 °C; ^{1}H NMR (Me_2SO-d_6) δ 6.1 (br s, 2 H, NH_2), 7.45–7.93 (m, 15 H, Ar H). Anal. Calcd for $C_{19}H_{17}N_2PS$: C, 67.79; H, 5.05; N, 8.32; P, 9.21; S, 9.51. Found: C, 67.71; H, 4.96; N, 8.09; P, 9.29; S, 9.51.

***N*-[(*P*,*P*,*P*-Triphenylphospha-λ⁵-azenyl)thiocarbonyl]-*P*,*P*,*P*-triphenylphospha-λ⁵-azene (18b).** The same procedure described above for **17b** but using 20 mmol each of TPP and DAD was employed. The product was purified by column chromatography (silica gel, 30% ethyl acetate in petroleum ether) and recrystallized from petroleum ether (60–80 °C): yield 3.1 g (73%), mp 159 °C; ^{1}H NMR δ 7.35–7.8 (m, Ar H). Anal. Calcd for $C_{37}H_{30}N_2P_2S$: C, 74.48; H, 5.07; P, 10.38. Found: C, 74.29; H, 5.10; P, 10.60.

***N*-[(*P*,*P*,*P*-Triphenylphospha-λ⁵-azenyl)carbonyl]-*P*,*P*,*P*-triphenylphospha-λ⁵-azene (18a).** The same procedure described above was used with urea (0.60 g, 10 mmol), TPP (5.24 g, 20 mmol), and DAD (3.48 g, 20 mmol) in anhydrous THF (60 mL). The product was recrystallized from ethanol: yield 2.7 g (46%), mp 202 °C; ^{1}H NMR (Me_2SO-d_6) δ 7.4–7.9 (m, Ar H). Anal.

Calcd for $C_{37}H_{30}N_2P_2O$: C, 76.54; H, 5.20; N, 4.83; P, 10.67. Found: C, 76.40; H, 5.08; N, 4.80; P, 10.55.

***N*-[(*P*,*P*,*P*-Triphenylphospha-λ⁵-azenyl)sulfonyl]-*P*,*P*,*P*-triphenylphospha-λ⁵-azene (18c).** The same procedure described above was used with sulfamide (0.96 g, 10 mmol). The product was washed several times with THF and then recrystallized from ethanol: yield 5.2 g (84%), mp 243–244 °C (lit.[18] 245–246 °C and 242–244 °C); ^{1}H NMR δ 7.5–8.1 (m, Ar H); ^{31}P NMR (Me_2SO-d_6) δ 8.56.

Reaction of Bis(diphenylphosphino)methane (8) with Urea and DAD. To a mixture of bis(diphenylphosphino)methane (8; 1.02 g, 2.7 mmol) and urea (0.16 g, 2.7 mmol) in 10 mL of dry THF was added a solution of DAD (0.91 g, 5.2 mmol) in 5 mL of THF, under argon. The mixture was stirred at room temperature for 24 h and then refluxed for 0.5 h. The insoluble material (0.07 g) was filtered and identified as urea. Column chromatography of the residue after removal of the solvent [silica gel, ethyl acetate–methanol (0.5%)] gave several fractions as follows: DH_2D, 0.66 g, mp 131–132 °C, urea, 0.05 g, mp 115–130 °C, 0.53 g (40%) of [(*N*-cyano-*P*,*P*-diphenylphospha-λ⁵-azenyl)-methyl]diphenylphosphine oxide (11): mp 190–191 °C, ^{31}P NMR ($CDCl_3$) δ 23.96 (d, J = 12.1 Hz), 22.98 (d, J = 12.0 Hz); ^{1}H NMR and IR spectra as above. Anal. Calcd for $C_{26}H_{22}N_2OP_2$: C, 70.90; H, 5.04; N, 6.36. Found: C, 70.87; H, 5.36; N, 6.48. The final fraction, 0.46 g (38%), was identified as bis(diphenylphosphino)methane dioxide (12): mp 181–183 °C (lit.[20] mp 181–183 °C); ^{31}P NMR ($CDCl_3$) δ 25.20; ^{1}H NMR ($CDCl_3$) δ 3.53 (t, 2 H, CH_2, J = 14.6 Hz), 7.2–8.0 (m, 20 H, Ar H); IR (KBr) $\bar{\nu}$ 1435 (P—C), 1185 and 1197 (P=O), 1117.

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Synthesis and Complexing Properties of Diaza-Crown and Cryptand Ligands with Inward-Facing Phenolic Groups

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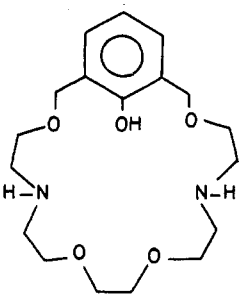
Novel diaza-crown and cryptand molecules with inward-facing phenolic group are synthesized and found to exhibit enhanced complexation of transition and heavy metal cations when compared with closely related cyclic and bicyclic ligands that do not possess this auxiliary binding site.

Crown ethers (macrocyclic polyethers) that contain a 1,3-xylyl unit and bear intraannular functionality at the 2-position have been prepared in several laboratories. The intraannular groups include hydroxyl,[1-5] hydroxymethyl,[6,7] methoxy,[1-5] methoxymethyl,[1,2] allyloxy,[5] carboxylic acid,[6,7] methoxycarbonyl,[6,7] amino,[8] nitro,[8] and sulfinic acid[9] substituents. Of particular interest has been the influence of such inward-facing groups upon metal ion complexation. Diaza-crown ethers and cryptands are efficient complexing agents for a variety of transition and heavy metal cations.[10]

We now report syntheses of the first 1,3-xylyl unit based diaza-crown ether and cryptand ligands with inward-facing phenolic units, **1** and **2**, respectively, and assessment of their complexation behaviors with Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) in water.



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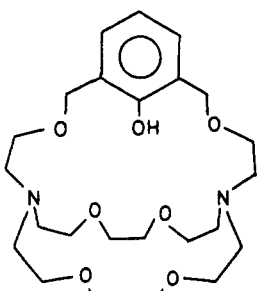

2

Results and Discussion

Synthesis. The preparation of diaza-crown ether **1** was accomplished by the method outlined in Scheme I.

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